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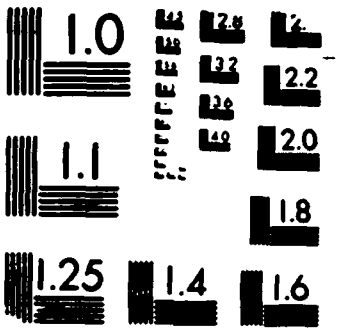

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NEW SYNTHETIC APPROACHES TO BORON HYDRIDE TRANSFORMATIONS

FINAL REPORT

LARRY G. SNEDDON

January 25, 1988

U. S. ARMY RESEARCH OFFICE

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UNIVERSITY OF PENNSYLVANIA

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This project was concerned with the development of new synthetic routes to polyhedral boron cage compounds. This work resulted in new methods for the preparation of several important classes of compounds, including new mono-, di-, and tetra-carbon carboranes, multi-cage boranes and carboranes, and large single cage boranes.

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Summary of Scientific Goals and Results

Stable, high-boron content materials, such as the polyhedral boranes and carboranes, are known to have a great number of potential practical applications, including uses in polymers, burning-rate accelerators and medical therapies. However, because of the low yield, non-selective synthetic methods which have generally been used to obtain these types of compounds their actual utilization has been limited. The main goal of our work which was sponsored by the Army Research Office was to investigate the fundamental processes involved in boron hydride transformations and to apply these results to the development of new high yield, low energy, selective synthetic routes for polyhedral boron compounds.

In our work we have taken several different approaches to these problems and these have resulted in major advances toward the goals outlined above. Important results have included (1) the discovery of a new pathway to higher cage materials via boron-boron coupled multicage compounds (2) the development of new synthetic routes to mono-, di-, and tetra-carbon carboranes and (3) the synthesis and structural characterizatin of a variety of new metalla-borane, -carborane and -thiaborane complexes with unusual properties.

Results of this project have been described in detail in the publications and progress reports listed below:

Publications:

1. J.J. Briguglio and L.G. Sneddon, "Metal Atom Synthesis of Metalla-Boron Clusters 6. Synthesis and Structural Characterization of a Coupled Diborane-Metallacarborane Cluster: 5:1',2'-[1-(η-C_5H_5)Co-2,3-$(Me_3Si)_2C_2B_4H_3$][B_2H_5]" *Organometallics*, 1985, *4*, 721-726.

2. R.J. Micciche, P.J. Carroll and L.G. Sneddon, "Metal Atom Synthesis of Metalla-Boron Clusters 7. Synthesis and Structural Characterization of an Open-Cage Triple-Decker Metallathiaborane Cluster: 4,6-(η-C_5H_5)$_2Co_2$-3,5-$S_2B_2H_2$" *Organometallics*, 1985, *4*, 1619-1623.

3. E.W. Corcoran, Jr. and L.G. Sneddon, "Transition Metal Promoted Reactions of Boron Hydrides 7. Platinum Bromide Catalyzed Cage Growth and Dehydrocoupling Reactions of Diborane with Small Polyhedral Carboranes and Boranes: Synthesis of a New *Arachno* Carborane, 5,6-$C_2B_6H_{12}$, and the Diborane-Coupled Compounds 2:1',2'-[1,6-$C_2B_4H_5$][B_2H_5] and 2:1',2'-[B_5H_8][B_2H_5]. *J. Amer. Chem. Soc.*, 1985, *107*, 7446-7450.

4. J.J. Briguglio and L.G. Sneddon, "Metal Atom Synthesis of Metalla-Boron Clusters 8. Synthesis of New Cobalt, Iron and Nickel Clusters Derived From 2,6-$C_2B_7H_{11}$. Structural Characterizations of 2-[η^6-$C_6(CH_3)_3H_3$]Fe-1,6-$C_2B_7H_9$, 6-[η^6-$C_6(CH_3)_3H_3$]Fe-9,10-$C_2B_7H_{11}$ and 5,7,8-$(CH_3)_3$-11,7,8,10-[η^3-$C_4(CH_3)_4H$]$NiC_3B_7H_7$", *Organometallics*, 1986, *5*, 327-336.

5. E. W. Corcoran, Jr. and L.G. Sneddon, "Palladium and Platinum Promoted Reactions of Polyhedral Boranes and Carboranes" Advances in Boron and the Boranes, VCR: New York, 1987.

6. M. G. L. Maribelli and L.G. Sneddon, "Transition Metal Promoted Reactions of Boron Hydrides 8. Nickel Promoted Alkyne Insertion Reactions: A New Synthesis of the Four-Carbon Carborane 4,5,7,8-$R_4C_4B_4H_4$" *Organometallics*, 1986, *5*, 1510-1511.

7. J. J. Briguglio, P. J. Carroll, E. W. Corcoran, Jr., and L. G. Sneddon, "Structural Characterization and Cage-Condensation Reactions of the Coupled-Cage Borane, 1:2'-$[B_5H_8]_2$: New Routes to Higher Single-Cage Boranes and Carboranes" *Inorg. Chem.* 1986, *25*, 4618-4622.

8. J. S. Beck, A. P. Kahn, L. G. Sneddon "New Synthetic Routes to the Small *closo*-Carboranes 2,3- and 2,4-$R_2C_2B_5H_5$" *Orgamometallics*, 1986, *5*, 2552-2553.

9. R. L. Ernest, W. Quintana, R. Rosen, P. J. Carroll and L. G. Sneddon, "Reactions of Decaborane(14) with Silylated Acetylenes: Synthesis of the New Mono-Carbon Carborane, 9-$(Me)_2S$-7-$(Me_3Si)_2HC$-$CB_{10}H_{12}$" *Organometallics*, 1987, *6*, 80-88.

10. W. Quintana, R. L. Ernest, P. J. Carroll and L. G. Sneddon "Synthesis of Metalla-Boron Clusters Derived From the Mono-Carbon Carborane 9-$(CH_3)_2S$-7-$[((CH_3)_3Si)_2CH]CB_{10}H_{11}$" *Organometallics* 1988, *7*, 166-172.

11. L. G. Sneddon "Transition Metal Promoted Reactions of Polyhedral Boranes and Carboranes" *Pure Appl. Chem.*, 1987, *59*, 837-846.

12. M. G. L. Mirabelli and L. G. Sneddon "Transition Metal Promoted Reactions of Boron Hydrides 9. Cp*Ir Catalyzed Reactions of Polyhedral Boranes and Acetylenes." *J. Am. Chem. Soc.* 1988, *110*, 449-453.

13. S. O. Kang and L. G. Sneddon "Metal Atom Synthesis of Metalla-Boron Clusters 9. Synthesis and Structural Characterization of iso-8-$(\eta$-$C_5H_5)CoB_{17}H_{21}$" *Inorg. Chem.*, accepted.

14. S. O. Kang, P. J. Carroll and L. G. Sneddon "Metal Atom Synthesis of Metalla-Boron Clusters 10. Synthesis and Structural Characterization of (η^6-Arene)Thiaferraborane Clusters" *Organometallics*, accepted.

15. J. S. Beck and L. G. Sneddon "Reactions of *nido*-2,3-$Et_2C_2B_4H_6$ with Triethylammine-alane: Syntheses of New Small Cage Aluminacarboranes" *J. Am. Chem. Soc.*, accepted.

16. S. O. Kang and L. G. Sneddon "Improved Synthetic Routes to the Polyhedral Thiaboranes $SB_{10}H_{12}$ and SB_9H_{12}" *Inorg. Chem.*, submitted.

17. J. S. Beck, W. Quintana and L. G. Sneddon "Synthesis and Structural Characterization of the First Seven-Vertex *nido*-Carborane Anion: 3,4-$Et_2C_2B_5H_6^-$", *Organometallics*, submitted.

Progress Reports:

No.

1. 1/1/85-6/30/85
2. 7/1/85-12/31/85
3. 1/1/86-6/30/86
4. 7/1/86-12/31/86
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Participating Scientific Personnel

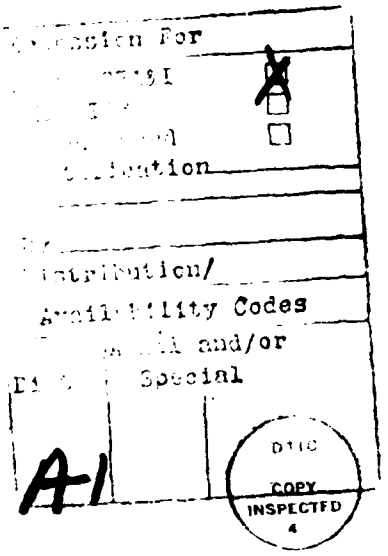
Larry G. Sneddon, Principal Investigator

Graduate Students

Ned Corcoran
Kalid Mazighi
Mario Mirabelli
William Quintana
Sang Oak Kang

Postdoctoral

James Briguglio



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